JAPANESE [JP,2000-159850,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the polyacetal copolymer which has advanced toughness and was excellent also in thermal stability.
[0002]
[Description of the Prior Art]A polyacetal copolymer has the mechanical physical property which balance was able to take, and outstanding fatigue characteristics-proof, Since it excels in character, such as heat resistance, chemical resistance, an electrical property, and slidability, and excels also in molding workability, it is used for wide range uses, such as a machine part, autoparts, and an electric electronic component, as engineering plastics. However, toughness is insufficient for many uses.
[0003]The trial which adds thermoplastic elastomer, such as a urethane system, an ester system, and an olefin system, from the former to polyacetal resin, and improves shock resistance has been carried out. However, there is a problem that the high rigidity and chemical resistance which are the advantages of

PORISE tar acid resin are spoiled in exchange for the improvement in toughness in this method, and, usually a use is limited. The polyacetal molding material which grows into JP,6-199972,A from the polyacetal copolymer of the small ultrahigh molecular weight of a melt flow index and a conventional additive is proposed. Even if this molding material does not add thermoplastic elastomer, it has high toughness.
It is possible to avoid the problem by the above-mentioned thermoplastic-elastomer addition.
However, although this molding material can be satisfied in respect of toughness, in order for thermal stability to run short and to present practical use, it is required to improve heat stability.
[0004]Although polyacetal resin is processed into a Plastic solid and is generally used by injection molding or extrusion molding, if the melt flow index of resin becomes small, melt viscosity will go up, and it becomes difficult to process it by the usual process condition. Therefore, although molding temperature will be raised and melt viscosity will be lowered and processed, if molding temperature is raised, PORISE tar acid resin will decompose, formaldehyde occurs and the problem that this adheres to a metallic mold at the time of injection molding (mold deposit), or worsens the surrounding environment occurs. The generated formaldehyde oxidizes and formic acid generates, and polymer backbone will be cut by this formic acid and it will fall into the vicious circle that low molecule quantification of polymer occurs or formic acid promotes decomposition of polymer further.
[0005]Therefore, high thermal stability is especially required of polyacetal resin of the small ultrahigh molecular weight of a melt flow index. The thermally unstable portion which exists in the Pori Atar copolymer conventionally for the improvement in thermal stability of a polyacetal copolymer Although carrying out melting hydrolysis and stabilizing a [-$(OCH_2)_n$-OH radical] with an extrusion machine etc. under existence of water, methanol or ammonia, amines, etc. has been performed, In the stabilization method of these former, the high thermal stability required of the polyacetal copolymer of ultrahigh molecular weight cannot be attained. In the stabilization method of these former, the problem that decomposition of polymer backbone takes place and polymer carries out low molecule quantification during stabilizing treatment is also generated. It is presumed that it is because the problem which the melt flow index described above since this had insufficient heat stability although one or less thing did not exist occurs in the commercial polyacetal resin in which thermoplastic elastomer is not added and it cannot use for a actual fabricating operation.

[0006]
[Problem(s) to be Solved by the Invention]Having high toughness, there is a technical problem of this invention in providing the polyacetal copolymer with little decomposition which was very much excellent in thermal stability, and its constituent also under a severe process condition at the same time it maintains advanced rigidity.
[0007]
[Means for Solving the Problem]As a result of this invention persons' inquiring wholeheartedly, it is a line polyacetal copolymer which are 1.0g/10 minutes or less in a melt flow index (MFI) as a molecular weight, And only when this polyacetal copolymer passes a decomposition solvent wiping removal of a specific unstable end piece shown below, it finds out that an aforementioned problem is solvable and comes to complete this invention.
[A decomposition solvent wiping removal of an unstable end piece] At least the 4th class ammonium compound of a kind of expressed with a following general formula (1), Convert into quantity of nitrogen of the 4th class ammonium compound origin expressed with a following formula (2) to total weight of a polyacetal copolymer and the 4th class ammonium compound, and under 0.05 - 50 weight ppm existence, More than the melting point of a polyacetal copolymer heat-treats, where melting of the polyacetal copolymer is carried out at temperature of 260 ** or less.
[0008]
$[R^1R^2R^3R^4N^+]_nX^{-n}$ (1)

(R^1, R^2, R^3, and R^4 among a formula) Respectively independently, An unsubstituted alkyl group of the carbon numbers 1-30. Or substituted alkyl group;. An aryl group of the carbon numbers 6-20; An aryl group of aralkyl group; or the carbon numbers 6-20 by which an unsubstituted alkyl group or a substituted alkyl group of the carbon numbers 1-30 was replaced by an aryl group of the carbon numbers 6-20 of at least one piece An unsubstituted alkyl group of the carbon numbers 1-30 of at least one piece. Or an alkyl aryl group replaced with a substituted alkyl group is expressed, and an unsubstituted alkyl group or a substituted alkyl group is straight chain shape, branched state, or annular. A substituent of the above-mentioned substituted alkyl group is halogen, a hydroxyl group, an aldehyde group, a carboxyl group, an amino group, or an amide group. As for the above-mentioned unsubstituted alkyl group, an aryl group, an aralkyl group, and an alkyl aryl group, a hydrogen atom may be replaced by halogen. n expresses an integer of 1-3. X expresses

acid residue of a hydroxyl group or carboxylic acid of the carbon numbers 1-20, hydro acid other than hydrogen halide, oxo acid, inorganic thio acid, or organic thio acid of the carbon numbers 1-20.

[0009]Px14/Q (2)

(P expresses quantity (ppm) to an oxymethylene copolymer of the 4th class ammonium compound, and total weight of the 4th class ammonium compound among a formula, 14 is an atomic weight of nitrogen and Q expresses a molecular weight of the 4th class ammonium compound.)

Hereafter, this invention is explained in detail. First, as for a melt flow index (MFI) of a polyacetal copolymer of this invention, it is indispensable that they are 1.0g/10 minutes or less. 0.8g/10 minutes or less of MFI(s) are 0.5g/10 minutes or less more preferably. MFI(s) are 0.2g/10 minutes or less most preferably. If MFI exceeds 1.0g/10 minutes, improvement in toughness is not enough.

[0010]A polyacetal copolymer can be manufactured by carrying out copolymerization of a trioxane, cyclic ether, and/or the cyclic formal under at least one sort of existence of a cation activity catalyst. As an example of cyclic ether and/or cyclic formal, ethyleneoxide, propylene oxide, 1,3-dioxolane, trio KISEPAN, 1,4-butanediol formal, etc. are mentioned. Especially, 1,3-dioxolane is the most suitable comonomer, in order to obtain a polyacetal copolymer which it is copolymerizable, and are MFI1.0g/10 minutes or less, and was excellent also in heat stability also with a small amount of cation activity catalysts. 0.02-15-mol% of the amount of these comonomers used is desirable to a trioxane, and is still more desirable. [0.1-10-mol% of] As long as it is necessary because of molecular weight regulation of a polyoxymethylene copolymer, a suitable regulator, for example, methylal etc., may be used.

[0011]If impurities which have active hydrogen (hydrogen of OH) contained in a trioxane or comonomer, such as water, methyl alcohol, and formic acid, exist in large quantities, when these will carry out a chain transfer reaction at the time of a polymerization, Low molecule quantification of produced polymer takes place, and MFI1.0g/an ultrahigh-molecular-weight copolymer for 10 minutes made into the purpose of this invention becomes is hard to be obtained. When impurities which have active hydrogen (hydrogen of OH), such as water, methyl alcohol, and formic acid, carry out a chain transfer reaction, it is an unstable terminal part at the time of a polymerization. A [-$(OCH_2)_n$-OH radical] generates and the thermal stability of a polyacetal copolymer falls. Then, in order to reduce low molecule quantification at the time of a

polymerization, and generation of an unstable terminal part, there is the necessity of reducing concentration of an impurity which has active hydrogen, such as water in a trioxane or comonomer, methyl alcohol, and formic acid, as much as possible by distillation, adsorption, etc. It is preferred that impurity concentration which has active hydrogen shall be converted into concentration of water practical, and the sum density shall be 20 ppm or less to the total quantity of a trioxane and comonomer. In the case of methyl alcohol, 0.28 time of methyl alcohol concentration, and in the case of formic acid, it is specifically [conversion to water concentration] obtained by [of formic acid concentration] increasing 0.20 times.

[0012]As a polymerization catalyst, cation activity catalysts, such as Lewis acid, proton acid and its ester, or an anhydride, are preferred. As Lewis acid, a halogenide of boric acid, tin, titanium, Lynn, arsenic, and antimony is mentioned, and boron trifluoride, a tin tetrachloride, titanium tetrachloride, phosphorus pentafluoride, phosphorous pentachloride, antimony pentafluoride and its complex compound, or a salt is specifically mentioned, for example. As an example of proton acid, its ester, or an anhydride, the Park Rolle acid, trifluoromethanesulfonic acid, and Park Rolle acid-3rd class butylester, acetyl par chlorate, trimethyl oxonium hexafluorophosphate, etc. are mentioned. Boron trifluoride especially; a coordination complex compound of an organic compound and boron trifluoride containing boron trifluoride hydrate; and an oxygen atom, or a sulfur atom is preferred, and, specifically, boron trifluoride diethylether and boron trifluoride di-n-butyl ether can be mentioned as a good example.

[0013]Generally, the amount of the polymerization catalyst used in composition of polyacetal takes into consideration a rate of polymerization and a molecular weight of output, and is decided. The suitable amount range of the polymerization catalyst used of not less than 3 ppm 30 ppm or less is not less than 5 ppm 15 ppm or less preferably on the basis of generation weight of this polyacetal copolymer concretely for obtaining a polyacetal copolymer which are MFI1.0g of this invention/10 minutes or less, and was excellent also in heat stability. A catalyst amount said here is not that for which it asked from a ratio of a reaction component prepared at the time of a polymerization, but is the value which was regarded as having analyzed an actually obtained constituent and boron trifluoride having been used as a polymerization catalyst, was converted, and was calculated.

[0014]For example, when a catalyst is reduced extremely and polymerization operation is performed, yield of resin falls, and when a catalyst amount per generation resin increases on the contrary, a cause can be known with this measuring method.

When the amount of the polymerization catalyst used is less than a suitable range, a problem which is not preferred practically that a polymerization yield falls and productivity falls greatly occurs. When the amount of the polymerization catalyst used exceeds a suitable range, in 1.0g/an ultrahigh-molecular-weight polyacetal copolymer for 10 or less minutes, MFI of this invention becomes is hard to be obtained by decomposition of polymer which a side reaction at the time of a polymerization increased and generated. Polymer degradation is promoted by polymerization catalyst which remained and heat stability of polymer gets worse. As a polymerization method, although there is no restriction in particular, mass polymerization can be mentioned and this mass polymerization may be any of a batch type and continuous system, for example. This mass polymerization has a common method of obtaining solid massive polymer with advance of a polymerization using a monomer in a molten state.

[0015]An end piece thermally unstable to a polyacetal copolymer obtained by the above polymerization Since a [-$(OCH_2)_n$-OH radical] exists, practical use cannot be presented if it remains as it is. Then, although it is required to carry out a decomposition solvent wiping removal of an unstable end piece, in this invention, it is indispensable to perform a decomposition solvent wiping removal of a specific unstable end piece shown below. Under at least one sort of existences of the 4th class ammonium compound expressed with a following general formula (1), a specific decomposition solvent wiping removal [of an unstable end piece] of more than the melting point of a polyacetal copolymer is 260 ** or less in temperature, and where melting of the polyacetal copolymer is carried out, it is heat-treated.

[0016]

$[R^1R^2R^3R^4N^+]_nX^{-n}$ (1)

(R^1, R^2, R^3, and R^4 among a formula) Respectively independently, An unsubstituted alkyl group of the carbon numbers 1-30. Or substituted alkyl group;. An aryl group of the carbon numbers 6-20; An aryl group of aralkyl group; or the carbon numbers 6-20 by which an unsubstituted alkyl group or a substituted alkyl group of the carbon numbers 1-30 was replaced by an aryl group of the carbon numbers 6-20 of at least one piece An unsubstituted alkyl group of the carbon numbers 1-30 of at least one piece. Or an alkyl aryl group replaced with a substituted alkyl group is expressed, and an unsubstituted alkyl group or a substituted alkyl group is straight chain shape, branched state, or annular. A substituent of the above-mentioned substituted alkyl group is halogen, a hydroxyl group, an aldehyde group, a carboxyl group, an amino group, or an amide group. As for the

above-mentioned unsubstituted alkyl group, an aryl group, an aralkyl group, and an alkyl aryl group, a hydrogen atom may be replaced by halogen. n expresses an integer of 1-3. X expresses acid residue of a hydroxyl group or carboxylic acid of the carbon numbers 1-20, hydro acid other than hydrogen halide, oxo acid, inorganic thio acid, or organic thio acid of the carbon numbers 1-20.

[0017]The 4th class ammonium compound used for this invention, If expressed with the above-mentioned general formula (1), there will be no restriction in particular, but R^1 in a general formula (1), R^2, R^3, and R^4 respectively independently, It is preferred that they are an alkyl group of the carbon numbers 1-5 or a hydroxyalkyl group of the carbon numbers 2-4, among these especially a thing whose at least one of R^1, R^2, R^3, and the R^4 is a hydroxyethyl group is still more preferred. Specifically Tetramethylammonium, tetraethylammonium, Tetrapropylammonium, tetra-n-butyl ammonium, Sept Iles trimethylammonium, Tetradecyl trimethylammonium, 1,6-hexa methylenebis (trimethylammonium), Decamethylene-bis-(trimethylammonium), trimethyl 3-chloro-2-hydroxypropyl ammonium, Trimethyl (2-hydroxyethyl) ammonium, triethyl (2-hydroxyethyl) ammonium, TORIPUROPIRU (2-hydroxyethyl) ammonium, tri-n-butyl (2-hydroxyethyl) ammonium, Trimethyl benzylammonium, triethyl benzylammonium, TORIPURO pill benzylammonium, tri-n-butylbenzyl ammonium, Trimethyl phenyl ammonium, triethylphenyl ammonium, Hydroxide, such as trimethyl 2-oxy ethylammonium, monomethyl trihydroxy ethylammonium, monoethyl trihydroxy ethylammonium, OKUDADESHIRUTORI (2-hydroxyethyl) ammonium, and tetrakis (hydroxyethyl) ammonium; Chloride. Hydro acid salts, such as bromate and fluoric acid; Sulfuric acid, nitric acid, phosphoric acid, carbonic acid, boric acid, Chloric acid, iodine acid, silicic acid, perchloric acid, a chlorous acid, hypochlorous acid, chlorosulfuric acid, Thio acid salts, such as oxo acid salt; thiosulfuric acid, such as amidosulfuric acid, disulfuric acid, and Tripoli phosphoric acid; carboxylate, such as formic acid, acetic acid, propionic acid, butanoic acid, isobutyric acid, pentanoic acid, caproic acid, caprylic acid, capric acid, benzoic acid, and oxalic acid, etc. are mentioned. Especially, a salt of hydroxide (OH^-), sulfuric acid (HSO_4^-, SO_4^{2-}), carbonic acid (HCO_3^-, CO_3^{2-}), boric acid ($B(OH)_4^-$), and carboxylic acid is preferred.

Formic acid, acetic acid, and especially propionic acid are preferred among carboxylic acid. These 4th class ammonium compound may be used independently, and may be used combining two or more sorts. In addition to the above-mentioned

4th class ammonium compound, even if it uses together amines etc. which are the decomposition accelerators of a publicly known unstable end piece, such as ammonia and triethylamine, it does not interfere at all.

[0018]converting quantity of the 4th class ammonium compound to be used into quantity of nitrogen of the 4th class ammonium compound origin expressed with a following formula (2) to total weight of a polyacetal copolymer and the 4th class ammonium compound -- 0.05 - 50 weight ppm -- it is 1 - 30 weight ppm preferably.

Px14/Q (2)

(P expresses concentration (weight ppm) to a polyoxymethylene copolymer of the 4th class ammonium compound among a formula, 14 is an atomic weight of nitrogen and Q expresses a molecular weight of the 4th class ammonium compound.)

Decomposition removing speed of an unstable end piece falls that an addition of the 4th class ammonium compound is less than 0.05 weight ppm, and if 50 weight ppm is exceeded, a color tone of a polyacetal copolymer after decomposition removal of an unstable end piece will get worse.

[0019]A decomposition solvent wiping removal of an unstable end piece of this invention is attained by heat-treating, where melting of the polyacetal copolymer is carried out at temperature of 260 ** or less as for more than the melting point. Although there is no restriction in particular in a device to be used, heat-treating using an extrusion machine, a kneader, etc. is preferred. Formaldehyde generated in decomposition is removed under decompression. There are no restrictions in particular in an addition method of the 4th class ammonium compound, and there are a method of adding a polymerization catalyst as solution at a process of being deactivated, a method of blowing upon polyacetal copolymer powder generated by polymerization, etc. If it is the variety which performs combination of a filler or a pigment using an extrusion machine etc. in what is necessary being to just be added at a process of heat-treating a polyacetal copolymer, and pouring in into an extrusion machine **** even if it uses which addition method, This compound may be installed to a resin pellet and unstable end removal operation may be carried out with a subsequent compounding operation.

[0020]Unstable end removal operation is possible also for carrying out, after a polymerization catalyst in a polyoxymethylene copolymer obtained by polymerization makes it deactivated, and can also be carried out, without deactivating a polymerization catalyst. A method of carrying out neutralization inactivation of the polymerization catalyst in solution of basicity, such as amines, as inactivation operation of a polymerization

catalyst can be mentioned as an example of representation. After heating under an inert gas atmosphere at temperature below the melting point and carrying out volatilization reduction of the polymerization catalyst, without being deactivated in a polymerization catalyst, it is also an effective method to perform this unstable end removal operation.

[0021]By a decomposition solvent wiping removal of the above specific unstable end piece, a polyacetal copolymer in which an unstable end piece hardly exists and which was very much excellent in thermal stability can be obtained. Since polymer backbone decomposes and polymer molecular weight hardly falls during processing like a conventional method according to the decomposition solvent wiping removal of this unstable end piece, in order to obtain an ultrahigh-molecular-weight polyacetal copolymer, it is a very convenient method. A melt flow index of this invention to 1.0g/an ultrahigh-molecular-weight polyacetal copolymer for 10 or less minutes. Mobility and rigidity of polymer can be raised without a melt flow index's mixing a line polyacetal copolymer and/or a line polyacetal homopolymer exceeding 1.0g/10 minutes, and spoiling the toughness of polymer greatly.

[0022]A melt flow index of a polyacetal copolymer of this invention to be used 0.1-1.0g/10 minutes, As for a melt flow index of a line polyacetal copolymer to mix and/or a line polyacetal homopolymer, it is preferred to mix so that a rate of a polyacetal copolymer of 10-300g/10 minutes, and this invention may be 30% of the weight or more. It is more preferred from the ease of carrying out of molding to carry out a melt flow index of a polyacetal resin constituent produced by mixing in 1.0g/10 minutes or more.

[0023]Especially since it is dramatically excellent in thermal stability after mixing to use a polyacetal copolymer pass a decomposition solvent wiping removal of a specific unstable end piece of this invention as a line polyacetal copolymer to mix and/or a line polyacetal homopolymer, it is preferred. It is also possible for there to be no restriction in particular in a mixing method, for example, to mix each pellets simply, and to process it into a predetermined Plastic solid with an injection molding machine etc. as it is, and, It is same to the toughness of polymer and rigidity which were obtained even if it is also possible to process it into a predetermined Plastic solid with an injection molding machine etc. and it used which method, after carrying out melting kneading of each pellets with an after-mixing extrusion machine etc. and obtaining a pellet.

[0024]A melt flow index of a line polyacetal copolymer used for mixing and/or a line polyacetal homopolymer, What is necessary

is for what is necessary to be just to choose timely according to a use to be used, and just to choose polymer which has a high melt flow index to a fluid use demanded. It is also an effective method to choose a polyacetal copolymer whose low melting points, for example, the melting point, are 155 ** - about 160 ** to a fluid use demanded in addition to a melt flow index. It is an effective method that a linear polyacetal homopolymer or the melting point is high, for example, the melting point chooses a not less than 167 ** polyacetal copolymer to a use as which rigidity is required. Anyway, a melt flow index of this invention to 1.0g/an ultrahigh-molecular-weight polyacetal copolymer for 10 minutes. A melt flow index by a method of mixing a line polyacetal copolymer and/or a line polyacetal homopolymer exceeding 1.0g/10 minutes. It is possible to obtain a polyacetal resin constituent with various toughness, rigidity, mobility, and thermal stability simple according to a use.

[0025]By blending a suitable additive agent with a polyacetal copolymer or a polyacetal resin constituent of this invention according to a use, a polyacetal resin constituent excellent in toughness with which practical use can be presented, and heat stability can be obtained. suitable -- to polyacetal copolymer 100 weight section as concrete, (A) A polymer or a compound containing an antioxidant and formaldehyde reactive nitrogen, At least one sort of a formic acid supplementary agent, weathering (light) stabilizer, and a mold release (lubricous) agent 0.1 to 10 weight section, and the (B) reinforcing agent, A conducting material, thermoplastics, and a polyacetal resin constituent that contains zero to 60 weight section, and the (C) paints 0 - five weight sections for at least one sort of thermoplastic elastomer can be mentioned.

[0026]As an antioxidant, a hinder TOFE Norian system antioxidant is preferred. Specifically, it is the n-octadecyl- 3, for example. -(3',5'-di-t-butyl-4'-hydroxyphenyl)- Propionate, n-octadecyl- 3 -(3'-methyl-5'-t-butyl-4'-hydroxyphenyl)- Propionate, n-tetradecyl- 3 -(3',5'-di-t-butyl-4'-hydroxyphenyl)- Propionate, 1,6-hexane ********-****- [3 -(3,5-di-t-butyl-4-hydroxyphenyl)-propionate], 1,4-butanediol bis- [3 -(3,5-di-t-butyl-4-hydroxyphenyl)- propionate], Triethylene glycol bis- [3 -(3-t-butyl-5-methyl-4-hydroxyphenyl)- propionate], Tetrakis [methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate] methane, 3, a 9-screw [2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl) propionyloxy}-1,1-dimethylethyl] 2,4,8,10-tetraoxaspiro (5, 5) undecane, N,N'-bis-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionylhexamethylenediamine, N,N'-tetramethylen bis-3-(3'-methyl-5'-t-butyl-4'-hydroxyphenol) propionyldiamine, N,N'-bis-[3-(3,5-di-t-butyl-4-hydroxyphenol)

propionyl] hydrazine, N **SARICHI roil N'-salicylidene hydrazine, 3-(N-Sarych roil) amino-1,2,4-triazole, N,N'-screw [2-{3-(3,5-di-t-butyl-4-hydroxyphenyl) propionyloxy} ethyl] oxyamide, etc. are mentioned.

[0027]Preferably, they are triethylene glycol bis- [3 -(3-t-butyl-5-methyl-4-hydroxyphenyl)- propionate] and tetrakis [methylene 3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate] methane. These antioxidants may be used by one kind and may be used combining two or more kinds. As an example of a polymer or a compound containing formaldehyde reactive nitrogen, Polyamide resin [, such as nylon 4-6, nylon 6, and nylon 6-6 and nylon 6-10, nylon 6-12, and Nylon 12,] and these polymers, for example, 6-, nylon 6 / 6 / 6-10, and nylon 6 / 6-12 grade can be mentioned. The Polly beta-alanine copolymer produced by polymerizing under existence of metal alcoholate in acrylamide and its derivative, and other vinyl monomers as a copolymer of acrylamide and its derivative, acrylamide and its derivative, and other vinyl monomers can be mentioned. A polymer containing these formaldehyde reactive nitrogen atoms may be used by one kind, and may combine two or more kinds.

[0028]As an example of a compound containing a formaldehyde reactive nitrogen atom which has an amino substituent, 2,4-diamino-sym-triazine, 2,4,6-triamino sym-triazine, N-butylmelamine, N-phenylmelamine, N,N-diphenylmelamine, N,N-diarylmelamine, N,N',N''-triphenylmelamine, MEREMU, a melon, MERAMU, benzoguanamine (2,4-diamino-6-phenyl-sym-triazine), Acetoguanamine (2,4-diamino-6-methyl-sym-triazine), 2,4-diamino-6-butyl-sym-triazine, 2,4-diamino-6-benzyloxy sym-triazine, 2,4-diamino-6-butoxy-sym-triazine, 2,4-diamino-6-cyclohexyl-sym-triazine, 2,4-diamino-6-chloro-sym-triazine, 2,4-diamino-6-mercapto-sym-triazine, 2,4-dioxy 6-amino-sym-triazine, 2-oxy-4,6-diamino-sym-triazine, N,N,N',N'-tetracyano ethyl BENZOBU anamine, SAKUSHINO guanamine, ethylene dimelamine, TORIGU anamine. They are melamine cyanurate, ethylene dimelamine cyanurate, TORIGU anamine cyanurate, AMMERIN, acetoguanamine, etc. These triazine derivatives may be used by one kind, and may be used combining two or more kinds.

[0029]As a formic acid supplementary agent, a polycondensation thing of the above-mentioned amino substitution triazine, amino substitution triazine, and formaldehyde, for example, a melamineformaldehyde polycondensation thing etc., can be mentioned. As other formic acid supplementary agents, hydroxide of an alkaline metal or alkaline-earth metals, an inorganic acid salt, carboxylate, or an alkoxide is mentioned. For example, they are carbonate of hydroxide, such as sodium, potassium,

magnesium, calcium, or barium, and the above-mentioned metal, an phosphate, silicate, borate salt, and carboxylate.
[0030]As carboxylic acid, saturation which has 10-36 carbon atoms, or unsaturation aliphatic carboxylic acid is preferred, and these carboxylic acid may be replaced by hydroxyl group. As aliphatic carboxylic acid, capric acid, undecylic acid, lauric acid, Tridecylacid, myristic acid, pentadecyl acid, pulmitic acid, heptadecylacid, Stearic acid, nonadecanoic acid, arachin acid, behenic acid, Wrigley serine acid, Cerinic acid, heptacosanoic acid, montanic acid, melissic acid, RAKUSERU acid, Undecylenic acid, oleic acid, elaidic acid, a cetoleic acid, erucic acid, Brassidic acid, sorbic acid, linolic acid, linolenic acid, arachidonic acid, PUROPI all acid, steer roll acid, 12-hydroxydodecanoic acid, 3-hydroxydecanoic acid, 16-hydroxyhexadecanoic acid, 10-hydroxyhexadecanoic acid, 12-hydroxyoctadecanoic acid, 10-hydroxy 8-octadecanoic acid, dl-erythro 9, 10-dihydroxyoctadecanoic acid, etc. are mentioned.
[0031]As a concrete example, Jimi Rith Ching acid calcium, dipalmitate calcium, Distearic acid calcium, calcium (myristic acid-pulmitic acid), calcium (myristic acid-stearic acid), and calcium (pulmitic acid-stearic acid) are mentioned, and they are dipalmitate calcium and distearic acid calcium especially preferably. In this invention, it may add simultaneously and two or more sorts of formic acid supplementary agents are not restricted at all. As for weathering (light) stabilizer said by this invention, one sort chosen from a benzotriazol system, an oxalic acid anilide system ultraviolet ray absorbent, and a hindered amine light stabiliser or two sorts or more are preferred.
[0032]As an example of a benzotriazol system ultraviolet ray absorbent, 2-(2'-hydroxy-5'-methyl-phenyl) benzotriazol, 2-(2'-hydroxy- 3', 5'-di-t-butyl-phenyl) benzotriazol, 2-[2'-hydroxy-3',5'-bis(alpha and alpha-dimethylbenzyl)phenyl] benzotriazol, 2-(2'-hydroxy-3',5'-di-t-amyl phenyl) benzotriazol, 2-(2'-hydroxy- 3', 5'-di-isoamyl phenyl) benzotriazol, 2'-hydroxy- 3' and 2-[5'-bis-(alpha and alpha-dimethylbenzyl) phenyl]-2H-benzotriazol, 2-(2'-hydroxy-4'-octoxy phenyl) benzotriazol, etc. are mentioned. As an example of an oxalic acid ARINIDO system ultraviolet ray absorbent, 2-ethoxy-2'-ethyl-oxalic acid-bis anilide, 2-ethoxy-5-t-butyl-2'-ethyl-oxalic acid-bis anilide, 2-ethoxy-3'-dodecyl oxalic acid bisanilide, etc. are mentioned. These ultraviolet ray absorbents may be used independently, respectively, and may be used combining two or more kinds.
[0033]As an example of a hindered amine light stabiliser, the 4-acetoxy 2, 2, and 6, 6-tetramethylpiperidine, 4-stearoyl oxy-2, 2, and 6, 6-tetramethylpiperidine, The 4-acryloyloxy 2, 2, and 6, 6-tetramethylpiperidine, 4-(phenylacetoxy)-2, 2 and 6, 6-

tetramethylpiperidine, 4-benzoyloxy 2, 2, and 6, 6-tetramethylpiperidine, 4-methoxy-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2, 2, and 6, 6-tetramethylpiperidine, The 4-cyclohexyloxy 2, 2, and 6, 6-tetramethylpiperidine, 4-benzyloxy 2,2,6,6-tetramethylpiperidine, the 4-phenoxy- 2, 2, and 6, 6-tetramethylpiperidine, 4-(ethyl carbamoyloxy)-2,2,6,6-tetramethylpiperidine, 4-(cyclohexylcarbamoyloxy)-2,2,6,6-tetramethylpiperidine, 4-(phenylcarbamoyloxy)-2,2,6,6-tetramethylpiperidine, bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)-carbonate, A bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)-oxalate, Bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)-malonate, Bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)-sebacate, A bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)-horse mackerel peat, Bis(2, 2, 6, and 6-tetramethyl 4-piperidyl)-terephthalate, 1,2-bis(2,2,6,6-tetramethyl 4-piperidyloxy)-ethane, alpha and alpha'-bis(2,2,6,6-tetramethyl 4-piperidyloxy)-p-xylene, a screw (the 2, 2, 6, and 6-tetramethyl 4-piperidyl tolylene 2 and 4-dicarbamate.) The bis(2,2,6,6-tetramethyl 4-piperidyl)-hexamethylene 1, 6-dicarbamate, A tris (2,2,6,6-tetramethyl 4-piperidyl)-benzene-1,3,5-TORIKARUBOKISHI rate, the tris (2,2,6,6-tetramethyl 4-piperidyl)-benzene- 1 and 3, 4-TORIKARUBOKISHI rate, 1-[2-{3-(3,5-di-t-butyl-4-hydroxyphenyl) propionyloxy} butyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionyloxy] 2, 2 and 6, and 6-tetramethylpiperidine. 1,2,3,4 - butane -- tetracarboxylic acid -- 1,2,2,6,6 - pentamethyl -- four - PIPERIJI -- Norian -- beta -- beta -- beta -- ' -- beta -- ' - tetramethyl one -- 3,9 - [-- 2,4,8,10 - tetraoxaspiro (5, 5) -- an undecane --] -- diethanol -- a condensate -- etc. -- mentioning -- having . The above-mentioned hindered amine light stabiliser may be used independently, respectively, and may be used combining two or more sorts.

[0034]A desirable weathering agent especially 2-[2'-hydroxy-3',5'-bis(alpha and alpha-dimethylbenzyl)phenyl] benzotriazol, 2-(2'-hydroxy-3',5'-di-t-buthylphenyl) benzotriazol, 2-(2'-hydroxy-3',5'-di-t-amyl phenyl) benzotriazol, Bis(1,2,2,6,6-pentamethyl 4-piperidinyl)sebacate, Bis-(N-methyl- 2, 2, and 6, 6-tetramethyl 4-piperidinyl)sebacate, Bis(2, 2, 6, and 6-tetramethyl 4-piperidinyl) sebacate, 1,2,3,4 - butane -- tetracarboxylic acid -- 1,2,2,6,6 - pentamethyl -- four - PIPERIJI -- Norian -- beta -- beta -- beta -- ' -- beta -- ' - tetramethyl one -- 3,9 - [-- 2,4,8,10 - tetraoxaspiro (5, 5) -- an undecane --] -- diethanol -- a condensate -- it is .

[0035]As a release agent, an olefin compound and silicone which are 10-500 are preferred, and use ** of alcohol, fatty acid and those fatty acid ester, polyoxy alkylene glycol, and the average degree of polymerization is carried out. As a reinforcing agent, an inorganic filler, glass fiber, a glass bead, and carbon fiber are mentioned. As a conducting material, conductive carbon black,

metal powder, or textiles are mentioned. As thermoplastics, polyolefin resin, an acrylic resin, styrene resin, poly car NETO resin, and an unhardened epoxy resin are mentioned. These denaturation things are also contained.

[0036]As an example of representation of thermoplastic elastomer, a polyurethane system elastomer, a polyester system elastomer, a polystyrene system elastomer, and a polyamide system elastomer are mentioned. Paints used by this invention are used in the range of zero to 5 weight section. If five weight sections are exceeded, thermal stability falls and it is not desirable. An inorganic pigment and an organic color are mentioned as paints. An inorganic pigment means what is generally used as an object for coloring of resin, for example, means zinc sulfide, titanium oxide, barium sulfate, titan yellow, cobalt blue, etc. Organic colors are paints, such as a condensation UZO system, an INON system, a FUROTA cyanine system, and monoazo.

[0037]

[Embodiment of the Invention]the following, an example, and a comparative example -- although this invention is explained more concretely, this invention is not limited at all by these. The term and measuring method in an example and a comparative example are as follows.

<Concentration of methyl alcohol, water, and formic acid> methyl alcohol was measured with the hydrogen flame ion detector with the gas chromatography equipped with the glass column filled up with the gas-chromatograph pack 55 (made by GL Sciences). It measured with the neutralization titration according [according to / in water / a curl Fischer moisture meter / formic acid] to a potassium hydrate.

[0038]The melt index (g/10min) was measured under conditions (190 ** and 2169 g) using MELT INDEXER made from an Oriental energy machine by <MI(melt index:g/10min)> ASTM-D1238.

After decomposing thermally a <boron trifluoride concentration (ppm)> polyacetal copolymer by 1 N-HCl, the fluorine concentration in a polyacetal copolymer was measured using the fluoride ion electrode (product made from HORIBA), and this was converted into boron trifluoride concentration.

[0039]A <rate of bending flexibility (kg/cm^2) and tensile elongation rate (%)> Toshiba Corp. make IS-80A injection molding machine is used, For 200 ** of cylinder-temperatures, and injection pressure $60kgf/cm^2$, and ejection time 15 seconds, for cool time 25 seconds, the specimen was created with the die temperature of 70 **, and the rate of bending flexibility was based on ASTM-D790, the tensile elongation rate was based on ASTM-

D638, and it measured.
A <IZOD impact strength (kg-cm/cm)> Toshiba Corp. make IS-80A injection molding machine is used, For 200 ** of cylinder-temperatures, and injection pressure 60kgf/cm^2, and ejection time 15 seconds, for cool time 25 seconds, the specimen was created with the die temperature of 70 **, and it measured the temperature of 23 **, and with the notch based on ASTM-D256.
[0040]Under a <formaldehyde gas generating speed (ppm/min)> nitrogen air current, it titrates and measures, after absorbing 230 ** and the formaldehyde gas emitted from a polyoxymethylene copolymer in 90 minutes in water. The measured total amount of formaldehyde was broken in 90 minutes, and (ppm/min) was calculated for the formaldehyde gas generating speed of the average per minute. It excels in thermal stability, so that formaldehyde gas generating speed is small.
<%, ppm> -- unless it refuses in particular, it is a weight reference altogether.
[0041]
[Work example 1]The biaxial paddle type continuation polymerization machine with a jacket which can let a heat carrier pass was adjusted to 80 **, and 1,3-dioxolane 444 g/Hr (it is 0.045 mol to 1 mol of trioxanes) was continuously added as the trioxane of 12 kg/Hr, and comonomer. The sum density of a trioxane, methyl alcohol in the mixture of 1,3-dioxolane, water, and formic acid was 12 ppm by water conversion concentration. As a polymerization catalyst, boron trifluoride di-n-butyl etherate polymerized by adding continuously cyclohexane solution 39.6 g/Hr of 1 % of the weight of boron trifluoride di-n-butyl etherate so that it might become 1.5x10 - 5 mol to 1 mol of trioxanes.
[0042]the polyacetal copolymer discharged from the mixer -- triethylamine 0.1% -- it supplied in solution and was deactivated in the polymerization catalyst. As opposed to polyacetal copolymer 100 weight section after the filtration after filtering the deactivated polyacetal copolymer with a centrifuge, Solution 1 weight section which contained hydroxylation Kolin formate (trimethyl 2-hydroxyethyl ammonium formate) as the 4th class ammonium compound was added, and after mixing uniformly, it dried at 120 **. The addition of hydroxylation Kolin formate was converted into the quantity of nitrogen, and was 20 ppm. The addition of hydroxylation Kolin formate was performed by adjusting the concentration of the hydroxylation Kolin formate in the solution containing the hydroxylation Kolin formate to add.
[0043]To polyacetal copolymer 100 weight section after this desiccation, as an antioxidant, 0.3 weight sections of 2,2'-methylenebises (4-methyl-t-butylphenol) were added, and the biaxial [with a vent] screw-type extrusion machine was supplied.

Water 0.5 weight-section addition was carried out to polyacetal copolymer 100 fused weight section in an extrusion machine, and the unstable end piece was decomposed in holding time 5 minutes in the extrusion machine preset temperature of 200 **, and an extrusion machine. The oxymethylene copolymer into which the unstable end piece was decomposed was devolatilized under the condition of vent degree-of-vacuum 20Torr, from the extrusion machine die part, was extruded as a strand and pelletized. The last polyacetal copolymer pellet was obtained to this pellet 100 weight section by mixing 0.15 weight sections and 0.05 weight sections of Nylon 66 for calcium stearate, and carrying out melting kneading with a single screw extruder with a vent further. The boron trifluoride concentration of the obtained polyacetal copolymer, MFI, IZOD impact strength, and formaldehyde gas generating speed were summarized in Table 1, and were shown. The rate of bending flexibility of this polyacetal copolymer is 23000kg/cm^2, and has practically sufficient rigidity.

[0044]

[Example 2, the 3 comparative examples 1-3] The kind of comonomer and the amount of the polymerization catalyst used which are used for a polymerization were changed, and the same experiment as Example 1 was conducted. MFI was adjusted by adding 0.0001-0.002 mol of methylal continuously to 1 mol of trioxanes as a chain transfer agent. The result was collectively shown in Table 1 together with Example 1. It is clear that 1g/the polyacetal copolymer's for 10 or less minutes MFI by which decomposition removal of the unstable end piece was carried out under the 4th class ammonium compound existence of this invention has high toughness and thermal stability.

[0045]

[Examples 4-6] Examples 4 and 5 changed the amount of the hydroxylation Kolin formate used, and conducted the same experiment as Example 1. Example 6 was changed into hydroxylation Kolin formate, and conducted the same experiment as Example 1 using hydroxylation triethylcholine formate (triethyl 2-hydroxyethyl ammonium formate). The boron trifluoride concentration of the obtained polyacetal copolymer, MFI, IZOD impact strength, and formaldehyde gas generating speed were summarized in Table 2, and were shown.

[0046]

[Comparative example 4] The completely same operation as Example 1 was performed except having decomposed the unstable end piece by the following methods, without adding hydroxylation Kolin formate. The result was collectively shown in Table 2 together with Examples 4-6.

[A decomposition removing method of an unstable part] To

polyacetal copolymer 100 weight section after desiccation, as an antioxidant, 0.3 weight sections of 2,2'-methylenebises (4-methyl-t-butylphenol) are added, The biaxial [with a vent] screw-type extrusion machine was supplied, three weight sections of triethylamine solution was added 20% to polyacetal copolymer 100 fused weight section in an extrusion machine, and the unstable end piece was decomposed in holding time 5 minutes in the extrusion machine preset temperature of 200 **, and an extrusion machine. Thermal stability is poor, if the 4th class ammonium compound is added and decomposition removal of an unstable part is not performed.

[0047]

[Examples 7 and 8] The pellet of Example 1 or Example 3 was mixed on the pellet obtained by the comparative example 2 at a rate shown in Table 3, injection molding was carried out to it as it was, and the tensile elongation rate was measured. The result was collectively shown in Table 3 together with the tensile elongation rate of the comparative example 1. By usually mixing the polyacetal of a molecular weight with the ultrahigh-molecular-weight polyacetal copolymer of this invention, mobility is improvable, maintaining high toughness (a tensile elongation rate is high).

[0048]

[Table 1]

表1

	ｺﾓﾉﾏｰ種類	三フッ化ホウ素濃度 (ppm)	MFI (g/10分)	IZOD衝撃強度 (kg・cm/cm)	ﾎﾙﾑｱﾙﾃﾞﾋﾄﾞｶﾞｽ発生速度 (ppm/min)
実施例1	1,3-ｼﾞｵｷｿﾗﾝ	11.2	0.10	30.4	3.8
実施例2	1,3-ｼﾞｵｷｿﾗﾝ	10.5	0.45	25.4	3.5
実施例3	1,3-ｼﾞｵｷｿﾗﾝ	11.3	0.76	20.3	4.0
比較例1	1,3-ｼﾞｵｷｿﾗﾝ	9.5	1.5	9.7	3.7
比較例2	1,3-ｼﾞｵｷｿﾗﾝ	11.0	9.8	6.5	4.1
比較例3	ｴﾁﾚﾝｵｷｻｲﾄﾞ	34	2.3	7.2	14.8

表2

	第4級ｱﾝﾓﾆｳﾑ化合物の種類	第4級ｱﾝﾓﾆｳﾑ化合物の使用量(窒素換算:ppm)	三フッ化ホウ素濃度 (ppm)	MFI (g/10分)	IZOD衝撃強度 (kg・cm/cm)	ﾎﾙﾑｱﾙﾃﾞﾋﾄﾞｶﾞｽ発生速度 (ppm/min)
実施例4	水酸化ｺﾘﾝ蟻酸塩	1	11.3	0.10	29.8	4.1
実施例5	水酸化ｺﾘﾝ蟻酸塩	42	11.2	0.10	30.7	3.9
実施例6	水酸化ﾄﾘｴﾁﾙｺﾘﾝ蟻酸塩	20	11.1	0.10	30.0	3.5
比較例4	−	−	11.4	0.15	26.9	20.3

表3

	超高分子ｺﾎﾟﾘﾏｰのMFI (g/10分)	超高分子ｺﾎﾟﾘﾏｰの割合(%)	混合するﾎﾟﾘﾏｰのMFI (g/10分)	混合後のMFI (g/10分)	引張伸度(%)	ﾎﾙﾑｱﾙﾃﾞﾋﾄﾞｶﾞｽ発生速度 (ppm/min)
実施例7	0.10（実施例1ﾎﾟﾘﾏｰ）	40	9.8(比較例2ﾎﾟﾘﾏｰ)	1.5	170	3.8
実施例8	0.76（実施例3ﾎﾟﾘﾏｰ）	70	9.8(比較例2ﾎﾟﾘﾏｰ)	1.8	160	3.9
比較例1	−	−	−	1.5(比較例1単独)	80	3.7

[0049]

[Effect of the Invention]The melt flow index MFI pass the decomposition solvent wiping removal of the unstable end piece under existence of the specific 4th class ammonium compound of this invention has toughness and thermal stability with expensive

1.0g/polyacetal copolymer for 10 or less minutes, and its constituent.

[Translation done.]